

O(1A)—P(1)—O(2A)	102.8 (2)	O(1B)—P(2)—O(2B)	101.9 (2)
O(1A)—P(1)—O(3A)	116.1 (2)	O(1B)—P(2)—O(3B)	116.7 (2)
O(1A)—P(1)—O(4A)	112.3 (2)	O(1B)—P(2)—O(4B)	112.5 (2)
O(2A)—P(1)—O(3A)	111.6 (2)	O(2B)—P(2)—O(3B)	111.2 (2)
O(2A)—P(1)—O(4A)	106.6 (2)	O(2B)—P(2)—O(4B)	106.7 (2)
O(3A)—P(1)—O(4A)	107.0 (2)	O(3B)—P(2)—O(4B)	107.3 (2)
P(1)—O(2A)—C(2A)	122.5 (2)	P(2)—O(2B)—C(2B)	122.0 (2)
O(2A)—C(2A)—C(1A)	108.7 (3)	O(2B)—C(2B)—C(1B)	109.0 (3)
C(2A)—C(1A)—O(5A)	123.8 (3)	C(2B)—C(1B)—O(5B)	124.5 (4)
C(2A)—C(1A)—O(6A)	110.5 (3)	C(2B)—C(1B)—O(6B)	110.1 (3)
O(5A)—C(1A)—O(6A)	125.7 (4)	O(5B)—C(1B)—O(6B)	125.4 (4)
Ca—O(1A)—Ca ⁱⁱ	102.5 (1)	Ca—O(1B)—Ca ⁱ	103.1 (1)
O(1A)—Ca—O(1A ⁱ)	174.0 (1)	O(1A)—Ca—O(1B)	103.7 (1)
O(1A)—Ca—O(1B ⁱⁱ)	77.6 (1)	O(1A)—Ca—O(7)	98.7 (1)
O(1A)—Ca—O(8)	86.6 (1)	O(1A ⁱ)—Ca—O(1B)	76.7 (1)
O(1A ⁱ)—Ca—O(1B ⁱⁱ)	102.5 (1)	O(1A ⁱ)—Ca—O(7)	87.3 (1)
O(1A ⁱ)—Ca—O(8)	87.4 (1)	O(1B)—Ca—O(1B ⁱⁱ)	175.2 (1)
O(1B)—Ca—O(7)	88.8 (1)	O(1B)—Ca—O(8)	89.0 (1)
O(1B ⁱⁱ)—Ca—O(7)	86.4 (1)	O(1B ⁱⁱ)—Ca—O(8)	95.7 (1)
O(7)—Ca—O(8)	174.6 (1)		
O(1A)—P(1)—O(2A)—C(2A)	176.6 (5)		
O(3A)—P(1)—O(2A)—C(2A)	51.4 (5)		
O(4A)—P(1)—O(2A)—C(2A)	-65.1 (5)		
P(1)—O(2A)—C(2A)—C(1A)	-125.8 (5)		
O(2A)—C(2A)—C(1A)—O(5A)	0.2 (6)		
O(2A)—C(2A)—C(1A)—O(6A)	-178.8 (5)		
O(1B)—P(2)—O(2B)—C(2B)	-179.2 (3)		
O(3B)—P(2)—O(2B)—C(2B)	-54.2 (3)		
O(4B)—P(2)—O(2B)—C(2B)	62.6 (3)		
P(2)—O(2B)—C(2B)—C(1B)	128.8 (4)		
O(2B)—C(2B)—C(1B)—O(5B)	-1.2 (5)		
O(2B)—C(2B)—C(1B)—O(6B)	178.1 (4)		

Symmetry codes: (i) $-\frac{1}{2} + x, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

Table 6. Hydrogen-bonding geometry (Å, °) for compound (II)

D	H	A	H...A	D...A	D—H...A
O(4A)	H(4A)	O(3B ⁱ)	1.67 (4)	2.624 (3)	169 (4)
O(6A)	H(6A)	O(3B ⁱⁱ)	1.69 (4)	2.613 (3)	158 (5)
O(4B)	H(4B)	O(3A)	1.65 (4)	2.602 (3)	166 (4)
O(6B)	H(6B)	O(3A ⁱⁱⁱ)	1.63 (4)	2.585 (3)	166 (4)
O(7)	H(7)	O(5A ^{iv})	1.95 (5)	2.874 (3)	158 (5)
O(7)	H(7)	O(5B)	1.99 (4)	2.939 (3)	165 (5)
O(7)	H(7)	O(2B)	2.32 (4)	2.912 (3)	118 (5)
O(8)	H(8)	O(2A ^v)	2.37 (4)	2.938 (3)	116 (3)
O(8)	H(8)	O(5A ^v)	2.04 (4)	2.944 (3)	155 (4)
O(8)	H(8)	O(5B ^{vi})	2.22 (7)	2.843 (3)	121 (5)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 + x, y, 1 + z$; (iii) $x, y, z - 1$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - 1$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (vi) $x, y, z + 1$.

Colourless crystals of the title compounds were grown from aqueous solutions containing a 1:1 molar ratio of CaCl₂ or ZnCl₂ and phosphoglycolic acid. Furthermore, the Ca crystals were also obtained from stoichiometric water solution of CaO and phosphoglycolic acid.

For both compounds, data collection used *Kuma KM-4 Software* (Kuma Diffraction, 1989). Oscillation and Weissenberg photographs as well as preliminary diffractometer data collection suggested the isomorphism of the Zn salt with zinc(II) phosphoenolpyruvate dihydrate crystals. The refinement was started by using the published coordinates for heavy atoms of the Zn(PEP)₂·2H₂O crystal (Lis, 1992). The structure of the Ca salt was solved by the heavy-atom method. In both structures, the H atoms were found from difference maps and refined with constraints (O—H = 0.97 and C—H = 1.08 Å). Both structures were refined using *SHELX76* (Sheldrick, 1976)

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71510 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1054]

References

- Kuma Diffraction (1989). *Kuma KM-4 Software User's Guide*. Version 3.1. Kuma Diffraction, Wrocław, Poland.
- Lebioda, L., Stec, B., Brewer, J. M. & Tykarska, E. (1991). *Biochemistry*, **30**, 2823–2827.
- Lis, T. (1992). *Acta Cryst.* **C48**, 424–427.
- Lis, T. (1993). *Acta Cryst.* **C49**, 696–705.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1994). **C50**, 185–188

Dicalcium 1,4,5,8-Naphthalenetetracarboxylate Pentahydrate

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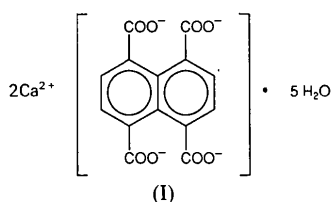
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Abstract

In the title structure, the 1,4,5,8-naphthalenetetracarboxylate anion possesses *2/m* symmetry with the twofold axis coincident with the central C—C bond of the naphthalene rings. The ten atoms comprising the naphthalene core have a mean deviation of 0.033 Å from the best least-squares plane describing these atoms, with the carboxyl C atom 0.395 (2) Å removed from the plane. The dihedral angle between the carboxylate plane and the least-squares plane of the naphthalene rings is 46.2 (3)°. The O—C—O angle of the carboxylate group, 121.13 (12)°, is smaller than normally expected, presumably due to the bidentate interaction with the Ca ion. The Ca ion is coordinated by eight O atoms: six carboxylate O atoms and two water O atoms. Because the Ca ion resides on a twofold axis there are only four independent Ca—O distances, which are in the range 2.368 (1)–2.681 (1) Å. In this structure, the organic anions are separated by Ca ions and water molecules such that there are no short-range organic–organic interactions. One of the water molecules separating the organic anions is not involved in coordination with Ca, and is disordered.

Comment

The structures of a series of hydrated Group IA salts of naphthalene-1,4,5,8-tetracarboxylic acid have been reported (Fitzgerald, Gallucci & Gerkin, 1991, 1992; Fitzgerald & Gerkin, 1993) as part of a continuing investigation into hydrogen bonding in the organic solid state. For this series of Group IA salts it was demonstrated that increasing the size of the cation had a small but discernible effect on the conformation of the carboxylate group as well as on the number and arrangement of the water molecules of hydration. The present study of the structure of dicalcium 1,4,5,8-naphthalenetetracarboxylate pentahydrate (I) provided an opportunity to evaluate the effect of changing the cation charge on the conformation of the organic anion and on the attendant hydrogen-bond network.



The molecular unit was found to possess $2/m$ symmetry with the Ca ion on the twofold axis ($0, y, \frac{1}{2}$) and C(4) on another ($0, y, 0$). Fig. 1 shows the organic anion and the numbering scheme with bond lengths and bond angles given on different asymmetric units. Fig. 2 illustrates the crystal packing.

The naphthalenetetracarboxylate anions in the structures of the Group IA salts cited above have inversion centers at the midpoint of the central bond of the naphthalene moiety. Although here the organic anion has $2/m$ symmetry, the pattern of bond lengths and angles for the naphthalene core is in good agreement with those of the Group IA structures. The ten atoms comprising the naphthalene core have a mean deviation of 0.033 Å from the best least-squares plane describing these atoms, with the carboxyl C atom 0.395 (2) Å removed from the plane. These values are closest to the corresponding values in the tetrapotassium structure (Fitzgerald & Gerkin, 1993) of the Group IA series. The dihedral angle between the C(1), O(1), O(2) carboxylate plane and the least-squares plane of the naphthalene moiety is 46.2 (3)°.

In the present study the two C—O bond lengths are found to be equal and the two C—C—O bond angles differ by less than 1.2°, a conformation expected for carboxylate groups. Both carboxylate O atoms are coordinated to a Ca ion, thus exhibiting a bidentate interaction as described by Einspahr & Bugg (1981). Significant features of such an interaction are: (a) a smaller than usual O—C—O angle;

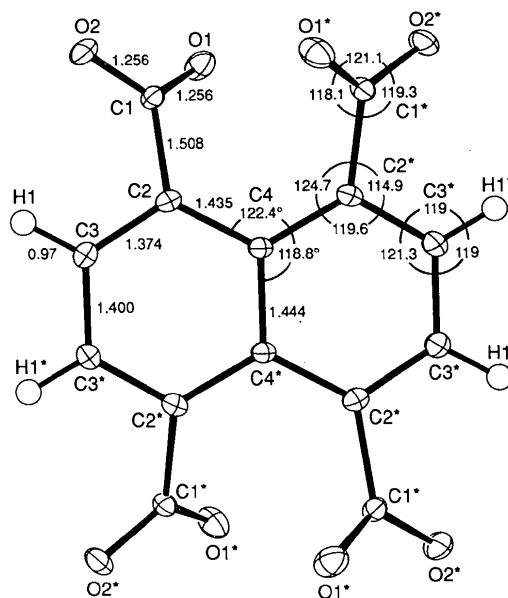


Fig. 1. An ORTEP (Johnson, 1976) drawing of the organic anion of the title structure showing the numbering scheme. The anion was found to have $2/m$ symmetry; bond lengths (Å) are given on one asymmetric unit and bond angles (°) on another. The maximum e.s.d. for non-H atoms is 0.003 Å for bond lengths and 0.1° for bond angles; for H(1), 0.02 Å for bond lengths and 1.0° for bond angles.

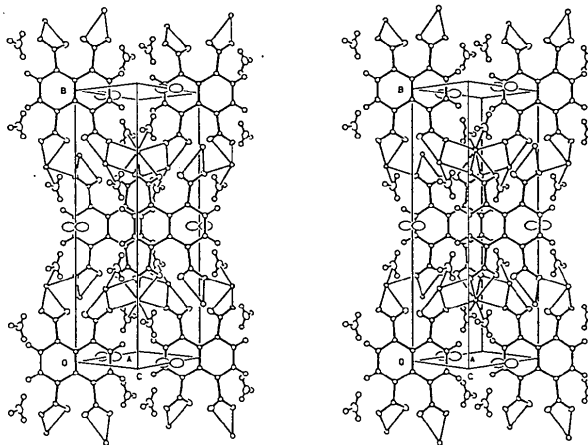


Fig. 2. An ORTEP (Johnson, 1976) stereoview of a unit cell of the title structure. Complete Ca coordination is shown for only two ions.

(b) Ca—O coordination distances larger than other Ca—O coordination distances; and (c) the Ca ion within 1 Å of the plane of the carboxylate group. All three features are exhibited by the present structure: the O—C—O angle, 121.13 (12)°, is smaller than the mean O—C—O angle for the Group IA structures, 125.1 (4)°; the two bidentate Ca—O distances are larger than the remaining two unique Ca—O distances (Table 2); and the Ca ion is found to be 0.749 (2) Å from the carboxylate plane.

The Ca ion is coordinated by eight O atoms: six carboxylate O atoms and two water O atoms. Because the Ca ion resides on a twofold axis, there are only four independent Ca—O distances. The bidentate interactions occur between Ca and O(1), O(2), O(1ⁱⁱ) and O(2ⁱⁱ), while monodentate interactions occur between Ca and O(2ⁱ) and O(2ⁱⁱⁱ). The range of Ca—O distances, 2.368 (1)–2.681 (1) Å, is similar to the ranges reported for other calcium salts of aromatic acids: calcium phthalate monohydrate, 2.303–2.595 Å (Schuckmann, Fuess & Bats, 1978), calcium terephthalate trihydrate, 2.350–2.642 Å (Matsuzaki & Iitaka, 1972), and calcium dihydrogenmellitate, 2.346–2.635 Å (Uchtman & Jandacek, 1980).

Two water-molecule O atoms were identified, these being O(3) at a general position and coordinated to Ca, and O(4), disordered near a 2/m site and not involved in Ca-ion coordination. Two H-atom positions were identified for O(3) which provided good hydrogen-bond geometry with O(1) and O(4) as acceptors. However, perhaps as a result of the disorder of the O(4) atom, a third H-atom position was identified for O(3) which provided three weak hydrogen-bond interactions with O(1), O(2) and a symmetry-related O(3) atom as acceptors. These three H-atom positions did not refine satisfactorily but were included in the final refinement with fixed parameters; no H atoms were included for O(4). A table describing the resulting water molecule geometry and hydrogen-bond parameters has been deposited as supplementary material.

Each organic anion is coordinated to four Ca ions through bidentate interactions and to four additional Ca ions through the monodentate interactions of O(2). A twofold axis (0, y, 0) is coincident with the central C—C bond of the naphthalene ring system and the least-squares plane of the naphthalene rings forms a 55° angle with the a axis. The O(3) water molecules, which complete the coordination around the Ca ion, and the O(4) water molecules occupy the space between organic ions. The separation of the organic anions by water molecules was also found to be a consistent structural feature in the Group IA series.

Experimental

Crystal data

[Ca₂(C₁₄H₄O₈)]·5H₂O

M_r = 470.44

Monoclinic

*C*2/*m*

a = 7.737 (2) Å

b = 18.634 (2) Å

c = 5.911 (2) Å

β = 97.67 (2)°

D_m = 1.87 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 14–15°

μ = 0.730 mm⁻¹

T = 296 K

V = 844.6 (3) Å³

Z = 2

D_x = 1.85 Mg m⁻³

Hexagonal plate

0.35 × 0.27 × 0.15 mm

Colorless

Data collection

Rigaku AFC-5S diffractometer

ω/2θ scans

Absorption correction:

empirical (six ψ scans)

T_{min} = 0.95, *T_{max}* = 1.00

2716 measured reflections

1275 independent reflections

1083 observed reflections

[*I* > 3σ(*I*)]

R_{int} = 0.013

θ_{max} = 30°

h = 0 → 10

k = 0 → 26

l = -8 → 8

6 standard reflections

monitored every 150

reflections

intensity variation: ±1.5%

Refinement

Refinement on *F*

R = 0.024

wR = 0.033

S = 1.502

1083 reflections

75 parameters

w = (2*FLP*)²/[σ_{cs}²(*I*) + (0.03)²]

(Δ/σ)_{max} < 0.01

Δρ_{max} = 0.38 e Å⁻³

Δρ_{min} = -0.19 e Å⁻³

Atomic scattering factors

from Cromer & Waber

(1974) for non-H atoms

and Stewart, Davidson

& Simpson (1965) for H

atoms

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Ca	0	0.27646 (2)	1/2	1.07 (1)
O(1)	-0.0631 (1)	0.17958 (6)	0.2251 (2)	1.60 (4)
O(2)	0.2205 (1)	0.18890 (5)	0.3203 (2)	1.47 (3)
O(3)	0.5982 (1)	0.14525 (7)	0.2180 (2)	2.30 (4)
O(4)	0.0351 (8)	1/2	0.0723 (8)	4.9 (3)
C(1)	0.0881 (2)	0.15399 (7)	0.2380 (2)	1.02 (4)
C(2)	0.1071 (2)	0.07586 (6)	0.1799 (2)	1.10 (4)
C(3)	0.2185 (2)	0.03756 (7)	0.3356 (2)	1.84 (5)
C(4)	0	0.03874 (8)	0	0.91 (5)

Table 2. Selected distances (Å) and angles (°) in the Ca-ion polyhedron of the title structure

Ca—O(1)	2.434 (1)	Ca—O(1 ⁱⁱ)	2.434 (1)
Ca—O(2)	2.681 (1)	Ca—O(2 ⁱⁱ)	2.681 (1)
Ca—O(2 ⁱ)	2.368 (1)	Ca—O(2 ⁱⁱⁱ)	2.368 (1)
Ca—O(3 ⁱ)	2.413 (1)	Ca—O(3 ⁱⁱⁱ)	2.413 (1)
O(1)—Ca—O(1 ⁱⁱ)	84.26 (5)	O(2)—Ca—O(2 ⁱⁱ)	105.02 (4)
O(1)—Ca—O(2)	50.62 (3)	O(2)—Ca—O(2 ⁱ)	125.41 (4)
O(1)—Ca—O(2 ⁱⁱ)	74.44 (4)	O(2)—Ca—O(2 ⁱⁱⁱ)	75.66 (4)
O(1)—Ca—O(2 ⁱ)	79.22 (4)	O(2)—Ca—O(3 ⁱ)	79.54 (4)
O(1)—Ca—O(2 ⁱⁱⁱ)	126.25 (4)	O(2)—Ca—O(3 ⁱⁱⁱ)	156.57 (3)
O(1)—Ca—O(3 ⁱ)	92.34 (4)	O(3 ⁱ)—Ca—O(3 ⁱⁱⁱ)	105.60 (6)
O(1)—Ca—O(3 ⁱⁱⁱ)	148.86 (4)		

Symmetry codes: (i) *x* - ½, ½ - *y*, *z*; (ii) -*x*, *y*, 1 - *z*; (iii) ½ - *x*, ½ - *y*, 1 - *z*.

Crystallization of the title compound was achieved by means of a silica gel growth according to procedures described by Henisch (1970). A solution of Ca(NO₃)₂ slowly diffused into a silica gel containing sodium 1,4,5,8-naphthalenetetracarboxylate to produce single crystals.

Unit-cell parameters were obtained from a symmetry-constrained least-squares fit. X-ray data were collected using scan widths of (1.6 + 0.35tanθ)° in ω, and a background to

scan time ratio of 0.5. The Bijvoet mate was measured for every 15th reflection throughout the intensity-data collection. No decay correction was applied but the data were corrected for Lorentz and polarization effects and for absorption; ψ -scan absorption data were taken at the end of data collection, the correction method being that of North, Phillips & Mathews (1968). Systematic absences (hkl , $h + k = \text{odd}$) were consistent with three space groups: $C2$, Cm and $C2/m$. Solutions were attempted in each. For the two non-centrosymmetric space groups, $C2$ and Cm , solutions exhibited high correlation coefficients and non-positive-definite displacement parameters, while refinement proceeded well for the centrosymmetric space group, $C2/m$ (No. 12); the latter was adopted. The direct-methods program *SHELXS86* (Sheldrick, 1985) produced an E map from which the initial positions of the Ca cation and the C and O atoms of the organic anion were determined. The positions of the water O atoms and the H atoms were subsequently identified using difference Fourier methods. The water molecule O(3) atom was found at a general position and refined normally. The water molecule O(4) atom was found at a $2/m$ site ($0, \frac{1}{2}, 0$) and refined with $B_{\text{eq}} = 13.5 \text{ \AA}^2$, indicating disorder. The disorder was then modeled by placing O(4) slightly off the twofold axis but still on the mirror. This model refined to give the smaller B_{eq} values listed in Table 1, and also a lower R value. [The disorder of O(4) was also present in the structures determined in $C2$ and Cm .] The Ca, O and C atoms were refined anisotropically and the ring H atoms refined isotropically using full-matrix least squares (*TEXSAN*; Molecular Structure Corporation, 1989). Following convergence, three of the top four peaks in the difference map were within 1.0 \AA of O(3) which suggested further disorder, possibly due to the disorder of O(4). Two H atoms were distributed over these three sites using occupancy factors determined from the relative peak heights on the difference map. These partial-occupancy H atoms, with fixed positional and displacement parameters, were included in the final refinement cycles. The maximum peak on the final electron density difference map was located near (0,0,0), approximately at the midpoint of the central bond of the naphthalene ring. The minimum peak was located near (0.55,0.20,0.16), approximately 1.2 \AA from O(3) and 2.1 \AA from Ca.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and hydrogen-bond geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71405 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1060]

References

- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Einspahr, H. & Bugg, C. E. (1981). *Acta Cryst.* **B37**, 1044–1052.

- Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1991). *Acta Cryst.* **C47**, 2315–2319.
Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1992). *Acta Cryst.* **C48**, 1430–1434.
Fitzgerald, L. J. & Gerkin, R. E. (1993). *Acta Cryst.* **C49**, 1287–1294.
Henisch, H. J. (1970). *Crystal Growth in Gels*. The Pennsylvania State Univ. Press, University Park, PA 16802, USA.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Matsuzaki, T. & Itaka, Y. (1972). *Acta Cryst.* **B28**, 1977–1981.
Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
Schuckmann, W., Fuess, H. & Bats, J. W. (1978). *Acta Cryst.* **B34**, 3754–3756.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Uchtman, V. A. & Jandacek, R. J. (1980). *Inorg. Chem.* **19**, 350–355.

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trans-Bisaquabis[1,2-bis(diphenylphosphino)ethane]technetium(I) Tetrphenylborate

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Abstract

The title compound, *trans*-bisaquabis[1,2-ethanediybis(diphenylphosphine)]technetium tetrphenylborate, [Tc(C₂₆H₂₄P₂)₂(H₂O)₂][B(C₆H₅)₄], consists of packed [Tc(H₂O)₂(dppe)₂]⁺ cations [dppe is 1,2-bis(diphenylphosphino)ethane] and tetrphenylborate anions. The Tc atom is coordinated in an octahedral environment. The two aqua ligands are in a *trans* arrangement with Tc—O distances of 2.307 (4) and 2.252 (4) Å and an O1—Tc—O2 angle of 175.7 (2)°. The equatorial Tc—P distances fall in the range 2.493 (2)–2.505 (2) Å.